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DEPARTMENT OF COMMERCE

UNITED STATES BUREAU OF MINES
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CHALK, WHITING, AND WHITING SUBSTITUTES

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OLIVER BOWLES

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DEPARTMENT OF COMMERCE - BUREAU OF MINES

CHALK, WHITING, AND WHITING SUBSTITUTES[1]

By Oliver Bowles[2]

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ORIGIN AND CHARACTER OF CHALK AND RELATED MATERIALS

Chalk is defined as a noncrystalline, soft, friable, fine-grained, light-colored type of limestone. It consists essentially of calcareous shells of minute organisms known as "foraminifera," although skeletal remains of molluscs, corals, and sponges are also present. Flint balls which are found so commonly in the chalk cliffs of Europe are regarded as segregations of the remains of certain organisms, such as radiolarians and sponges, that secrete siliceous shells or spicules. The famous chalk beds of northwestern Europe are of Upper Cretaceous age, a geological period that was particularly favorable for the development and multiplication of foraminifera.

The distinguishing physical characteristics of true chalk never have been fully defined; probably its noncrystalline and colloidal properties are most important. The properties of chalk, whiting, and whiting substitutes are not well understood, and much research is necessary before definite reasons may be ascribed for the behavior of these materials under various conditions of use.

The Bureau of Mines has undertaken a detailed study of chalk and similar materials to determine their exact properties and to establish a basis for classifying formations loosely designated as chalk occurring in various parts of the United States, but the results of this study will not be available for some months.

Whiting is a pulverized, purified, and carefully sized chalk. Whiting substitutes consist of finely ground limestone or dolomite, ground marble (marble flour), white marl, and chemically precipitated calcium carbonate.

SOURCES OF CHALK

Very little true chalk has been produced in the United States, domestic requirements being supplied from deposits in England, France, Belgium, and Denmark. A few years ago chalk was obtained from some American deposits; but very little, if any, of the present domestic production of pulverized calcium carbonate can be classed as true chalk. "Precipitated chalk" is a misnomer, for chemically precipitated calcium carbonate has physical properties quite different from those of true chalk.

CHALK DEPOSITS OF THE UNITED STATES

Chalks of Cretaceous age occur in many places, chiefly in the Middle Central and Southern States. Most of them contain high percentages of impurities such as clay and sand, but several occurrences of reasonable purity have been noted. Domestic chalks have been quarried for cement manufacture but have found limited use as whiting. If it can be demonstrated that some of these deposits contain true chalk comparing favorably with the imported product, a study of methods of purification and treatment might be justified.

Brief descriptions of the deposits are given in the following paragraphs. Most of the data on occurrences have been obtained from United States Geological Survey Bulletin 522, Portland Cement Materials and Industry in the United States, by E. C. Eckel, E. F. Burchard, and others, published in 1913. Reports giving further details are cited in footnotes.

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Alabama[3]

The Selma Chalk of Cretaceous age extends as a belt across Alabama, widening toward the west to a maximum of about 25 miles. It outcrops in many places along the Alabama River from Elm Bluff to Old Lexington Landing and along the Tombigbee River from Paces Landing almost to Moscow. A notable outcrop, about 930 feet in maximum thickness, appears at Selma. Most of the material is impure, and even the purer part which occurs in the lower beds of the formation contains not more than about 85 per cent calcium carbonate. It consists in part of foraminifera shells and is thus identified with true chalk; but most of the fossils found in it are described as molluscs, oyster shells, and other forms. During the World War it was quarried at Glendon and at Walker Springs, Clark County, and it is said that the purified product was quite satisfactory for manufacture of putty or for any other of the uses of true chalk.

Arkansas[4]

Important occurrences of chalk of Upper Cretaceous age have been noted in southwestern Arkansas, chiefly in Little River, Howard, Hempstead, and Clark Counties. The formation is divided into two parts. The lower series of beds, which outcrops near Rocky Comfort, White Cliffs, and Saline Landing, is known as the Annona member; and the upper, the Saratoga. Excellent exposures appear in several places; one, which overlooks Little River, is 115 feet thick above water level. Much of the chalk is massive, white, and somewhat friable. It can be broken into pieces by hand, but a hammer is required for pulverizing. The best material ranges from 85 to 93 per cent total carbonate.

The Saratoga member lies about 200 feet above the Annona, with clayey beds intervening. It has a maximum thickness of about 50 feet where complete sections have been found. In the numerous outcrops that extend from the vicinity of Saratoga near West Saline River in Hempstead County to Little Deciper Creek near Arkadelphia in Clark County the material is fairly uniform in character. It is more impure than the Annona beds, the best analyses showing less than 74 per cent total carbonate.

Colorado

Two Cretaceous limestone formations, the Niobrara and the Greenhorn, occur in Colorado just east of the Front Range in the vicinity of Fort Collins and Colorado Springs. The best material contains more than 90 per cent total carbonate, but it is a hard massive rock quite unlike chalk in physical character.

Iowa

According to Calvin[5] chalk of Cretaceous age (Niobrara group) occurs in western Iowa along the Sioux River between Sioux City and Hawarden, chiefly in Woodbury and Plymouth

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3 For more detailed descriptions see: Semmes, Douglas R., Oil and Gas in Alabama: Geol. Survey of Alabama Special Rept. 15, 1929, pp. 208-209; and Adams, George I., Butts, Charles, Stephenson, L. W., and Cooke, Wythe, Geology of Alabama: Geol. Survey of Alabama Special Rept. 14, 1926, pp. 237-240.

4 A detailed description of the Arkansas deposits is given by: Taff, J. A., The Chalk of Southwestern Arkansas, with Notes on Its Adaptability to the Manufacture of Hydraulic Cements: U. S. Geol. Survey Twenty-second Ann. Rept. Pt. 3, 1902, pp. 687-742.

5 Calvin, S., Cretaceous Deposits of Woodbury and Plymouth Counties, etc.: Iowa Geol. Survey Ann. Rept., vol. 1, 1893, pp. 147-161.

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Counties. It forms prominent bluffs near Westfield, Akron, and Hawarden. The beds ordinarily exposed are 20 to 30 feet thick, but probably a total thickness of 50 feet occurs. The chalk is made up largely of shells of an oysterlike lamillibranch identified as "Inoceramus." Foraminifera remains are recorded but are much less abundant. The rock is composed of varying proportions of chalk and limestone. The chalk is described as soft, white to buff in color, and more or less fossiliferous. Soft limestones are interbedded in places, although some beds several feet thick are quite free from the firmer limestone. The best of the material ranges from 86 to 95 per cent in total carbonate and is low in magnesium.

Kansas

Cretaceous limestones of the Niobrara formation, which is 750 to 800 feet thick, occur in a belt passing through the northwestern part of Kansas. According to Haworth[6], the rock when freshly quarried may be easily sawed into blocks and worked with chisel and hammer but becomes much harder by weathering. Evidently it could be pulverized without great difficulty; but, curiously enough, it has been used chiefly for fence posts, while minor quantities are employed as building stone. Analyses show a carbonate content of 90 to 92 per cent, with less than 1 per cent of magnesium carbonate. In a letter to the writer the Kansas Geological Survey states that the lower member, known as the "Fort Hays," which is 60 to 80 feet thick, contains very good-grade chalk. Individual beds have an average thickness of about 4 feet and are separated from each other by chalky shale beds which average about 1 foot in thickness. The upper and much thicker member, the Smoky Hill, is thin-bedded and contains greater amounts of shale.

Louisiana

Three occurrences of Cretaceous limestones in Louisiana have been described - the Winnfield, the Coochie Brake, and the Bayou Chicot. None is of chalklike consistency, and all are sufficiently consolidated to be used for building purposes. The Winnfield is highly crystallized and contains about 98 per cent calcium carbonate; the second deposit is sandy limestone. The Bayou Chicot deposit is very small. Although they belong geologically to the chalk formation these deposits apparently do not possess any of the characteristics of chalk.

Mississippi[7]

In northeastern Mississippi the Selma Chalk of Cretaceous age outcrops in a zone 10 to 30 miles wide. It crosses the Tennessee boundary, passes southward for some distance, turns eastward in Noxubee County, and extends into Alabama. In its southern outcrop the rock is 800 to 900 feet thick but thins to 250 feet in the vicinity of Corinth, Alcorn County. In a letter to the writer E. N. Lowe, director of the Mississippi Geological Survey, states it may scarcely be considered true chalk; rather it is soft argillaceous limestone much denser than typical chalk. The best of it contains 70 to 84 per cent of total carbonate with a magnesium content usually less than 1 per cent. Certain parts of the uppermost division, commonly known as "rotten limestone," may, however, contain more than 90 per cent of calcium carbonate, and by careful selection of purest occurrences chalk of good quality may possibly be obtained.

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6 Haworth, E., Mineral Resources for Kansas for 1897: Univ. Geol. Survey of Kansas Ann. Bull., 1898, pp. 75-76.

7 For more complete information see: Crider, A. F., Portland Cement Materials of Mississippi: Mississippi Geol. Survey Bull. 1, 1907.

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Montana

Cretaceous rocks of the Plains region throughout the eastern two-thirds of Montana contain lenses and concretions of limestone which have been used locally for lime burning. Apparently they are not adapted for use as chalk.

Nebraska

The Cretaceous deposits of Nebraska are similar to those of northwestern Kansas. The most promising source of chalk is a 50-foot lower bed of the Niobrara formation corresponding with the Fort Hays limestone of Kansas. Their tendency to weather to light yellow is a characteristic feature of the rocks. Owing chiefly to admixtures of clay the limestones vary greatly in composition. Representative analyses show a total carbonate content ranging from 67 to 96 per cent, with 1 per cent or less of magnesium carbonate. Cretaceous exposures occur extensively along the Missouri River and along the Republican Valley from Alma to a point near Superior.

North Dakota

The Niobrara limestone of Upper Cretaceous age occurs in North Dakota but is almost entirely concealed by a thick covering of glacial drift. No details as to its character are available.

Oklahoma

Cretaceous limestones occur in the southern part of the State. Some beds are soft, chalklike in consistency, and cream or white in color. They are probably low in magnesia, but no analyses have been obtained.

South Dakota

Niobrare (Cretaceous) chalk beds similar to those of Nebraska and Kansas occur in the southeastern part of the State. The chalk is exposed in many places along the bluffs of the Missouri River from Yankton to Chamberlain. Ward[8] states that it outcrops in various places east of the river and also as a more or less continuous band nearly encircling the Black Hills to the west. It has been found in digging wells in many widely separated parts of the State. Presumably, it underlies most of South Dakota and averages about 150 feet in thickness. It is similar in character to deposits of the same formation in Nebraska and Kansas, which have been described previously.

Tennessee

An extension of the Selma Chalk crosses from Mississippi into southern Tennessee, becoming thinner toward the north and disappearing entirely near Camden in Benton County. Its character has been described in the sections on Alabama and Mississippi chalks.

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8 Ward, Freeman, Chalk: South Dakota Geol. and Nat. Hist. Survey Circ. 6, 1919.

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Texas[9]

The Austin Chalk, which is the lower part of the Gulf series of Upper Cretaceous age, occurs as a well-defined belt in east-central Texas. From Red River in the northeastern part of the State it extends westward near Clarksville, Honeygrove, Paris, and Sherman. From Sherman it extends south and southwestward beneath Dallas, Waco, Austin, and San Antonio, terminating a little southwest of the latter city. The rock is white, friable limestone of chalklike consistency, although J. A. Udden, director of the Bureau of Economic Geology, Austin, Tex., states in a letter to the writer that it is not as soft or porous as the Niobrara chalk of western Kansas. It is 400 to at least 600 feet thick and in many places is remarkably uniform. Although interbedded with clays and shales in some localities certain beds are composed of nearly pure chalk. When freshly quarried the material may be cut easily with a handsaw. Under a microscope it shows the typical characteristics of chalk, including shells of foraminifera, molluscs, and other marine organisms. Air-dried exposures are brilliant white and after weathering scale off in large conchoidal flakes with earthy fractures. Analyses show a calcium carbonate content ranging from 70 to more than 90 per cent and very little magnesium. The chalk occurs in the most populous part of Texas, and quarry conditions are favorable. Similar chalky limestones occur in other members of the Cretaceous, notably the Edwards and Comanche Peak, the latter being nearly 100 feet thick. They have been used for lime manufacture near Austin.

Utah

A deposit of chalk not less than 40 acres in extent is reported about 50 miles from Delta in Millard County. A sample which was sent to the United States Bureau of Mines for examination closely resembles imported chalk. No further information regarding its extent or possibilities has been obtained, but the quality of the material would justify further investigation.

SUMMARY OF OCCURRENCES

From the above descriptions it appears that true chalk production of any consequence has been confined to Alabama. In other States, notably Arkansas, Iowa, Kansas, Mississippi, Nebraska, South Dakota, and Texas, further prospecting and testing may develop valuable supplies. The Cretaceous occurrences of Colorado, Louisiana, Montana, and North Dakota are unpromising as sources of chalk.

WHITING SUBSTITUTE PRODUCED FROM LIMESTONE

Whiting substitute in the form of finely pulverized limestone is reported to the United States Bureau of Mines from Arkansas, California, Georgia, Illinois, Michigan, Missouri, Nebraska, New Jersey, Ohio, Pennsylvania, and Tennessee. A few companies obtain it as a by-product at crushed-stone plants, but most of it is produced by those whose chief activity is the preparation of finely ground products. Marble flour is also produced, but returns from marble companies are very incomplete. The most important use of the limestone product is as rubber filler; smaller amounts are used for putty and paint. Very little is consumed in the calcimine trade, probably because crystalline or granular limestone has poorer covering qualities than the more amorphous chalk.

9 For more detailed information regarding the Austin Chalk see: Hill, R. T., Geology and Geography of the Black and Grand Prairies, Tex.: U. S. Geol. Survey Twenty-first Ann. Rept., pt. 7, 1901, pp. 329-336.

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Total production in 1929 was reported as 125,430 tons. Actual production was probably much greater because statistics relative to by-products are usually incomplete, and because some grinding companies do not own quarries and hence are not canvassed by the United States Bureau of Mines.

POSSIBLE UTILIZATION OF MARL DEPOSITS

Marl is an unconsolidated accumulation of impure calcium carbonate in fresh-water lakes and swamps. It results both from chemical precipitation and from actual mechanical deposition of calcareous shells of tiny animals and is usually mixed with clay and sand. Large deposits occur in Michigan, Indiana, Minnesota, and many other States. Some of the purer marls might possibly be used as whiting substitute, but the difficulty of finding sufficiently pure material and the cost of drying and other treatment discourage development for such purpose.

WHITING SUBSTITUTE PRODUCED AS A CHEMICAL PRECIPITATE

Some companies manufacture very pure calcium carbonate by a process of precipitation from a milk-of-lime suspension. This chemically controlled product finds special uses, notably as a dentifrice. Whiting substitute is also manufactured as a by-product at paper mills. Several companies dispose of this product chiefly as a rubber filler. Chemically precipitated calcium carbonate is obtained as a by-product of certain other chemical industries, notably in the recovery of basic magnesium carbonate from dolomite for the manufacture of pipe covering. Very little of this material finds commercial use.

GENERAL REQUIREMENTS OF WHITING SUBSTITUTES

In general, limestone flour that will successfully meet the requirements of fillers of a type like whiting or china clay should be ground finely and sized uniformly to about 300-mesh size. Chemical purity, though not essential, is desirable, as snow-white powder is most in demand. Each limestone deposit yields a whiting substitute with individual characteristics, the suitability of which for various uses can be determined only by actual tests.

In seeking a market for his product the manufacturer of whiting substitutes should be familiar with the many and varied uses of whiting, the more important of which are given in following paragraphs. This product may be employed in most of the applications for which true whiting is used, but for some uses substitutes have not been satisfactory.

USES OF WHITING

An important use is for calcimine and cold-water paints which contain about 80 per cent pure white whiting. An organic colloidal material is usually added. Crystalline limestone or marble is not sufficiently opaque to give a good covering effect, therefore true whiting is preferred for ceiling and wall coatings. Whiting is also used as an inert paint extender.

A second important use is for the manufacture of putty, which ordinarily consists simply of a mixture of 85 per cent whiting or whiting substitute with 15 per cent linseed oil; some putties also contain white lead. Specifications for putty manufacture require that the whiting shall contain not less than 95 per cent of calcium carbonate and shall be free

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from grit. It is generally conceded that whiting substitute will not make a "long" putty and can not, therefore, take the place of true whiting in this product. Recently, however, the claim has been made that "short" putty is preferable to "long" in glazing metal window sash. A "long" putty is one that has good stretching power, cohesiveness, and strength, while a "short" putty is more brittle. As a rule, whiting substitute has lower oil-absorption qualities than true whiting.

A third important use is as a raw material in ceramics. One function is to supply the calcium oxide component of glazes, enamels, and fluxed ceramic bodies. It is also an active fluxing agent when employed in small quantities in body mixtures. In glazes it may be applied as a raw ingredient, or it may be fritted or smelted with other glaze materials before application. True chalk, ground limestone, and precipitated lime carbonate are for the most part used interchangeably. Ceramic whitings are divided into two classes, both of which must contain not less than 97 per cent of total carbonates and not more than 2 per cent of SiO_2, 0.25 per cent of Fe_2O_3, and 0.1 per cent of SO_3. The magnesium carbonate content of class 1 is limited to 2 per cent and of class 2 to 8 per cent. Such classification is made because for certain uses a higher magnesium content is preferred.

Whiting is used as a filler in numerous products. True whiting low in magnesium is an important filler in rubber used for automobile tires. Some manufacturers use whiting substitutes, while others object to them. For certain types of rubber products, such as rubber soles and heels for shoes, substitute whiting has been found quite satisfactory. Whiting is used as a filler in oilcloth, window shades, and linoleum, sometimes forming 20 per cent of the latter product. Off-color whiting may be used as asphalt filler.

Whiting is used as a coating on glazed paper. In cigarette papers, some of which contain as much as 30 per cent of whiting, it performs quite a different function. The heat of burning tobacco drives off the carbon dioxide gas of the whiting, which opens the pores of the paper, thus promoting combustion without the formation of smoke.

Other products in which whiting is an important constituent include white ink, dressing for white shoes, picture-frame moldings, dolls, wire insulation, dyes, tooth paste, and fireworks. It is used for facing molds and cores used in brass casting and as a mild abrasive for polishing metals. Whiting is used in a small way in many industries, including structural iron, shipbuilding, locomotive works, file manufacture, explosives, medicines, printing and engraving, and the manufacture of shoes. It is also employed as a neutralizing agent in fermentation processes. For most of the purposes mentioned substitutes have been used with fair success. However, consumers differ considerably in their demands, most of them preferring true imported whiting.

PURIFICATION OF TRUE CHALK

Most of the whiting requirements of the United States are supplied by 12 plants which use imported European chalk as raw material. Six plants with a combined capacity of about 80,000 tons per year manufacture this material for sale; three are located in Boston, Mass., one at Bayonne, N. Y., one at Camden, N. J., and one at Philadelphia, Pa. The other six, having an estimated annual capacity of 39,000 tons, produce whiting for their own use; three of these plants are in New York, N. Y., one at Cartaret, N. J., one at Philadelphia, Pa., and one at Berkeley, Calif.

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In the older types of mills crude imported chalk is ground wet with edge runners. Material is brought to grinders in wheelbarrows or tram cars rather than by mechanical means, because flint balls which are associated with chalk are picked out by hand. The milklike suspension of ground chalk is conveyed to a series of settling tanks. Sand settles first and is discarded as waste. The material is graded according to the time required for settling. The highest grade of whiting remains in suspension longest. A cruder form of "commercial" whiting is obtained from the first tank. The overflow, which requires a longer period for settlement, supplies the "gilders" or "extra gilders" whiting deposited in the intermediate tanks. From these the overflow passes to a final tank, where after a still longer period of settlement a high-grade product known as "Paris white" is obtained. The overflow from the last tank is returned to the grinding mills. The whiting sludge from the settling tanks is either filter-pressed or evaporated to partial dryness; and final drying, which may occupy four weeks, is accomplished in heated chambers. The dried product is disintegrated, passed through a bolting machine, and packed in burlap bags of 50 or 100 pounds capacity.

Parsons[10] has described the equipment of a more modern type of mill. Crude lump chalk is passed through crushing rolls and disintegrated in a series of mullers. The sludge, consisting of about 11 parts of water to 1 part of solid, is conveyed to a series of modern bowl classifiers, hydroseparators, and thickeners. A large proportion of the water is thus removed. The pulp is dewatered further in a continuous filter, and final drying is accomplished in a rotary dryer which discharges to a storage bin from which the product is taken for disintegrating and bolting. This type of equipment yields only one grade of whiting at a time. Two or more complete units would be required to produce more than one grade simultaneously. The newer type of equipment greatly increases mill capacity, reduces labor requirements and production cost, and provides a very uniform and dependable product.

During the process of manufacture of whiting from chalk there is a shrinkage of about 20 per cent in weight; most of the loss is the water content of the crude chalk. Moisture in finished whiting ordinarily does not exceed 0.7 per cent.

The process of manufacture of whiting in England has been described briefly by Spence[11]. The industry is centered in Kent. The quarried chalk is placed in a 15-foot washing tank and pulverized by means of iron bars suspeneded from rotating arms. The slurry passes through a ¼-inch wire screen to a launder, which feeds it to eight trommels fitted with 180-mesh wire gauze. Only the material that passes through these screens is used for whiting. The fine slurry is conveyed to four series of settling pits with eight pits in each series. The slurry fills the first pit, flows over into the second, and so on until the eight are filled. The finer material is thus carried over and settles in the last four pits, the product of which is classed as No. 1 grade; that deposited in the first four is graded No. 2. The overflow from the pits is conveyed back to the washing tank. The whiting is dug out by hand and placed on drying floors which have heating flues beneath them. After it is dried for 36 hours it is taken by screw conveyor to a swing-hammer disintegrator which discharges to a bolting trommel. Some is single-bolted, and some double-bolted; the latter commands a higher price. Much of the chalk mined in Kent is shipped in crude form, chiefly to the United States.

10 Parsons, A. B., Dressing Crude Chalk by Modern Methods: Eng. and Min. Jour., vol. 116, No. 10, 1923, pp. 415-420.

11 Spence, Hugh S., The Manufacture of Whiting in England: Canadian Min. Jour., vol. 47, No. 38, 1926, p. 907.

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MANUFACTURE OF WHITING SUBSTITUTE FROM NATURAL ROCK

Limestone and marble are pulverized and graded by two processes - the wet method and the dry method. A typical wet process for manufacturing marble flour follows: Marble chips are ground wet in a pebble mill. The mill discharge is pumped to two settling cones, the settled product being returned in closed circuit to the pebble mill and the overflow conveyed to settling tanks. The sediment from the settling tanks, containing about 50 per cent of moisture, is dried in a type of drum drier which finds successful use in a number of southern plants. The drum, which preferably should be joined by welding to give a smooth surface, is 4 by 10 feet and revolves at 2½ r.p.m. Steam at 75 pounds pressure passes through a hollow shaft to the inside of the drum, beneath which is a rotating shaft with ⅜-inch iron pegs that splash the slurry mixture from a trough to the face of the drum. A series of scrapers, each about 1 foot long and held to the drum with springs, scrape off dried material to a screw conveyor. Lumps are broken up by an impact pulverizer. Drying capacity is 8 to 12 tons per drum per 24-hour day. Much of the whiting made from natural rock is prepared by some wet-ground process, because for certain uses, particularly for paint manufacture, water-ground material is preferred.

For dry-process grinding crushed rock is usually passed through a rotary drier and then ground by any one of a variety of processes. Rolls or impact mills of the swinging-hammer type are commonly used for coarser grinding, and impact pulverizers or pebble mills for final grinding. Sometimes grading by size is accomplished with air separators supplemented by vibrating screens. Air-floated material is satisfactory for many uses. Several mills are equipped for both wet and dry processes.

MANUFACTURE OF PRECIPITATED CALCIUM CARBONATE

Calcium carbonate obtained as a chemical precipitate (incorrectly called precipitated chalk) is manufactured on a large scale by two companies, one in Pennsylvania and one in West Virginia.

Calcium oxide (quicklime) and carbon dioxide are the raw materials. Lime is obtained by calcining pure limestone. The manufacture of this product is a very large industry, many thousands of tons being manufactured annually at plants located in nearly every State. Very pure lime is required for the manufacture of precipitated chalk. It is first slaked in water to form calcium hydroxide, commonly called "slaked lime", according to the following reaction: $CaO + H_2O = Ca(OH)_2$. Sufficient water is then added to make a thin milk-of-lime suspension. Milk of lime is sometimes called a solution; this is erroneous because calcium hydroxide is practically insoluble, one part dissolving in 760 parts of cold water. To remove all particles that do not disintegrate the milk of lime is passed through a fine screen.

Carbon dioxide gas, the second raw material, is manufactured by burning coke. Pure gas is desired; and to remove acids, dust, and moisture it is passed through "scrubbers" in the form of towers which contain limestone and excelsior. It is a peculiar circumstance that although precipitated calcium carbonate may be manufactured close to lime plants the carbon dioxide is not utilized, although hundreds of tons may pass off from the kilns every day. It is not used chiefly on account of its impurity.

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The milk-of-lime suspension, which resembles cream, is placed in upright cylinders about 18 feet high and 6 feet in diameter. Purified gas is blown in at the bottom of the cylinders, and as it comes in contact with lime particles a chemical combination takes place according to the formula $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$. Recarbonation requires two to three hours; completion of the reaction is determined by an indicator, such as phenolphthalein. Sometimes closed tanks equipped with agitators are used. The carbonation process must be carried out under exact and carefully controlled conditions. The precipitate of calcium carbonate is dewatered in filter presses, and the filter cakes are dried in hot-air tunnels at about 160° F. Dried cakes are pulverized and the finished article packed in paper-lined bags or barrels.

Commercial precipitated calcium carbonate is also manufactured as a by-product at paper mills. Large quantities of caustic soda are required, and this material is manufactured by treating lime with sodium carbonate, calcium carbonate being formed in the process. The chemical reaction may be expressed by the following formula: $CaO + Na_2CO_3 + H_2O = CaCO_3 + 2NaOH$. Calcium carbonate thus formed may contain a fraction of 1 per cent of alkali, which limits its use chiefly to that of rubber filler.

In the manufacture of basic magnesium carbonate from dolomite for use as pipe covering, finely divided calcium carbonate is obtained as a by-product. With careful manufacture from high-grade raw materials a pure product may be prepared, but little is now used. Calcium carbonate is formed as a by-product of numerous other industrial chemical processes, but very little is used as whiting substitute. Much of it is too impure for such use, and in some instances it is recovered for reuse in the industrial process concerned.

Three leading grades of precipitated calcium carbonate are recognized in the trade - extra light, light, and heavy; the principal difference is in density. Most of the production is of the light grade, and its principal use is in the manufacture of tooth paste. Individual manufacturers of tooth paste have their own standards of quality, and there are no exact or generally accepted specifications or methods of testing. Determination of the adaptability of a precipitated calcium carbonate for tooth-paste manufacture generally includes tests of density, sedimentation, wet bulk, alkalinity, and fineness. The domestic product meets with keen competition from imported material, which is obtained chiefly from England.

PRICES

The following prices, quoted from the Oil, Paint, and Drug Reporter of January 26, 1931, indicate the value of chalk, whiting, and related materials:

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Chalk, grinders', powdered, in barrels	Per ton	$12.00
Precipitated, car lots, extra light, casks	Per lb.	.03½ - .04½
heavy, casks	do do	.02 - .02¾
light, in casks	do do	.03¼ - .05¼
Whiting, domestic, in bags or barrels	Per 100 lbs.	1.00
English cliffstone, in bags	do do do	1.50
Limestone, ground, car lots, in bags	Per ton	6.00 - 10.00
Paris white, in bags	Per 100 lbs.	1.25 - 1.50
Imported, commercial, in bags		.85 - 1.50
ton lots, in bags	Per ton	14.00 - 24.00
gilders, bolted, in bags	Per 100 lbs.	1.25 - 1.50
extra bolted, in bags	do do do	1.40 - 1.60

PRODUCTION

Annual production of whiting substitute in the United States, as reported to the United States Bureau of Mines, is about 125,000 tons, with an average sales value of about $5.00 a ton at grinding plants. As previously stated, these figures are probably low because of incomplete returns.

IMPORTS

Imports of chalk and whiting are shown in the following table:

Chalk imported into the United States in 1930[12]

(General imports)

Country	Crude, not ground, bolted, precipitated, etc.		Cubes, blocks, sticks, disks, or other forms, and manufactures, n.s.p.f.[13]		Precipitated	
	Short tons	Value	Pounds	Value	Pounds	Value
Austria					860	$ 13
Belgium	3,289	$ 7,492				
Cuba	56	51				
France	86,435	67,297	5,695	$ 1,136	11,112	234
Germany			26,026	1,602	360,551	5,656
Italy			581	107	10,080	213
Japan			25	10		
Latvia					210,200	4,210
Mexico	28	280				
Netherland			858	56		
United Kingdom	25,402	32,710	11,762	694	4,373,762	101,588
	115,210	107,830	44,947	3,605	4,966,565	111,914

Whiting imported for consumption into the United States in 1930

Whiting, or Paris white, dry, ground, or bolted	Short tons	17,715	$91,818
Whiting, ground in oil (putty)	Pounds	240,742	4,194

12 Figures compiled by J. A. Dorsey of the U. S. Bureau of Mines from records of the Bureau of Foreign and Domestic Commerce.

13 Not specially provided for.

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EXPORTS

Exports of "Chalk and manufactures" for the year 1930 were 1,073,501 pounds valued at $138,442.

TARIFF

In the Tariff act of 1922, "Chalk crude, not ground, bolted, precipitated, or otherwise manufactured," was on the free list. If manufactured, however, it was dutiable according to the following provision: "Chalk or whiting or Paris white: Dry, ground, bolted or precipitated, 25 per centum ad valorem; ground in oil (putty) three-fourths of 1 cent per pound."

No change was made in the Tariff act of 1930 regarding unmanufactured chalk, crude material remaining on the free list (par. 1645). The provision for manufactured products was changed in the act of 1930 (par. 20) to read as follows: "Chalk or whiting or Paris white: Dry, ground, or bolted, four-tenths of 1 cent per pound; precipitated, 25 per centum ad valorem; ground in oil (putty), three-fourths of 1 cent per pound." Paragraph 20 further provides for chalk, etc. "put up in the form of cubes, blocks, sticks, or disks, or otherwise including tailors', billiard, red, and manufactures of chalk not specially provided for, 25 per centum ad valorem." Several of these products, however, consist of materials other than true chalk. Tailors' chalk, for example, is talc; red chalk may be earthy hematite or colored plaster of Paris; and black chalk may be carbonaceous clay.

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